Bimetallic catalysts supported on activated carbon for the nitrate reduction in water: Optimization of catalysts composition

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A B S T R A C T

The activities and selectivities of four pairs of bimetallic catalysts (Pd–Cu, Pt–Cu, Rh–Cu and Ir–Cu) supported on activated carbon were studied in order to optimize the metals composition for the reduction of nitrate in water with hydrogen. The catalytic tests were carried out in a semi-batch reactor, working at room temperature and pressure. The activity of the catalysts is quite different depending on the copper content. The maximum activity for the catalysts with 1% of the noble metal was obtained for 1%Rh–0.6%Cu, 1%Pd–0.6%Cu, 1%Pt–0.3%Cu and 1%Ir–0.3%Cu, with nitrate conversions after 5 h of reaction of 98%, 63%, 56%, and 55%, respectively. All these weight compositions correspond to an atomic ratio noble metal/copper close to 1. With the exception of the pair Ir–Cu, where the selectivity to ammonium is almost independent of the metals composition, for all the other cases it increases with the atomic copper content up to around 75%. The pair Rh–Cu was the most active among the bimetallic catalysts tested; however, significant amounts of ammonium are obtained. The nitrate conversions for the pairs Ir–Cu and Pt–Cu are similar but the former presents higher selectivities to ammonium. The pair Pd–Cu is the most selective in the transformation of nitrate to nitrogen.

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1. Introduction

The presence of nitrates in water is presently a common problem across Europe. Nitrate anion is potentially harmful because it can be transformed into nitrite in the human body, which can cause blue baby syndrome, and it is also a precursor of the carcinogenic nitrosamines [1–4]. For these reasons, the European Community limit values for nitrate, nitrite and ammonium concentrations in drinking water are, respectively, 50, 0.5 and 0.5 mg/L. However, for the discharge of wastewater the limits are 50 and 10 mg/L for nitrate and ammonium concentrations, respectively. The catalytic reduction is one of the most promising alternatives for nitrates removal without the drawbacks of the conventional methods [2,5–9]. This process consists in the reduction of nitrate to nitrogen over metallic catalysts in the presence of a reducing agent [1]. Nitrite as intermediate and ammonium as by-product are considered the major limitations of this process [9,10]. Studies of nitrate reduction have demonstrated that bimetallic catalysts are more efficient in comparison to monometallic. The noble metals Pd or Pt combined with the transition metals Cu or Sn, on different supports (alumina [5,8–15], silica [14], titania [16,17], activated carbon [1,3,4,18,19], polymers [20,21]) have been extensively studied and have been considered as the most actives and selectives for the reduction of nitrates but are still inadequate in terms of selectivity towards nitrogen. Moreover, additional studies are still necessary, mainly to optimize the formulation of the catalysts in order to develop an effective catalytic process for purifying water streams.

The catalytic properties of Pd–Cu catalysts were found to be sensitive to the ratio of these two metals. Both the nitrate removal activity and selectivity have a maximum at a specific palladium copper ratio, which can differ slightly with the support material and the preparation method used [5,22]. Epron et al. [23] demonstrated that the highest activity for the nitrate reduction is reached when 3%Pt–1%Cu and 1.7%Pd–0.5%Cu (weight percent) supported on alumina are used. Barrabés et al. [3], using activated carbon as a support, obtained 1%Pt–0.3%Cu and 1%Pd–1%Cu (weight percent) as the optimal metal proportions. Matatov-Meytal and Sheintuch [18] found that the 2%Pd–0.6%Cu (weight percent) is the optimal content when activated cloth is used as a support. These studies demonstrate that the selection of the support is important in this process, since the catalysts activity and selectivity are affected by the interaction between the active phase and the support.

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Carbon materials have been used for a long time in heterogeneous catalysis, because they can act directly as catalysts or, more important, they can satisfy most of the desirable properties required for a suitable support: inertness; stability under reaction and regeneration conditions; adequate mechanical properties; possibility to adapt their physical forms for a given reactor; and high surface area and porosity [24]. In addition, they allow easy recovery of the noble metals just by a simple burning process.

In a previous work [25] it was found that Pd–Cu, Pt–Cu, Rh–Cu and Ir–Cu were the most promising systems for nitrate reduction with hydrogen using activated carbon as support. Therefore, in this work, those systems were studied in detail in order to establish their best formulation. Although several results on the area of catalytic nitrate reduction have been described in the literature, principally using Pd–Cu but also Pd–Sn and Pt–Cu catalysts [1–3,6,14], as far as we know, only a recent report from other group of authors was presented using Rh–Cu, but supported on alumina [26], and there are no additional studies using the pair Ir–Cu. Our main goal is to establish a relationship between the ratio noble metal/copper and the activity and selectivity of the catalysts supported on activated carbon for the reduction of nitrates to nitrogen. This study has the additional advantage of comparing in a systematic way four different pairs noble metal/Cu, using the same support and experimental conditions, which allows a comprehensive comparison of the different noble metals used.

2. Experimental

2.1. Catalysts preparation

The active metals were supported on a commercial activated carbon NORIT GAC 1240 PLUS (ACo) ground to a particle diameter between 0.1 and 0.3 mm. According to the supplier specifications, it is an acid washed granular activated carbon, produced by steam activation. It has a neutral pH and offers good properties for water applications. The catalysts were prepared by incipient wetness co-impregnation, from aqueous solutions of the corresponding metal salts (H_2PtCl_6, $PdCl_2$, $Cu(NO_3)_2$, $RhCl_3$, $(NH_4)_3IrCl_6$). The amount of noble metal was maintained constant at 1 wt% and the Cu loadings tested for all systems were 0.1, 0.3, 0.6 or 1 wt%. The composition corresponding to 2 wt% of noble metal and 1 wt% of Cu was also evaluated. In addition, for the pairs Pd–Cu and Rh–Cu the compositions 1 wt% of noble metal and 2% or 5 wt% of Cu were also tested. The samples were dried at 100 °C for 24 h, calcined under a nitrogen flow at 400 °C for 1 h, and finally reduced at 400 °C in hydrogen flow for 3 h.

2.2. Catalysts characterization

Selected catalysts were characterized using different techniques: H_2 chemisorption, N_2 adsorption at 77 K, X-ray diffraction (XRD) and transmission electron microscopy (TEM). The chemisorption of H_2 was carried out at 30 °C and atmospheric pressure in an Altamira Instruments AMI-200 apparatus, using the pulse method. Pulses of 58 μL (from a calibrated loop) were successively injected in the carrier gas (25 Ncm³/min of Ar), which passes through a catalyst bed (150 mg), until saturation of the catalyst surface. The non-adsorbed hydrogen is measured with an online thermal conductivity detector. The textural characterization of the materials was based on the corresponding N_2 adsorption isotherms, determined at 77 K with a Coulter Omnisorp 100 CX apparatus. BET surface areas (S_{BET}) were calculated, as well as the micropore volumes (V_{micro}) and mesopore surface areas (S_{meso}) according to the t-method. A type IV deviation was noticed when the N_2 adsorption data were analyzed by the Dubinin method; the micropore volumes associated to small (W_{01}) and large micropores

(W_{02}) were determined, as well as the average small micropores width (L_1). XRD spectra of the catalysts were recorded in the range $2\theta = 20–90°$ on a Philips X'Pert MPD diffractometer (Cu-Kα, $\lambda = 0.15406$ nm). TEM micrographs were obtained using a LEO 906E microscope operating with an accelerating voltage of 120 kV.

2.3. Catalysts evaluation

The catalytic tests were carried out in a semi-batch reactor, equipped with a magnetic stirrer and a thermostatic jacket, at room temperature and atmospheric pressure, and using hydrogen as reducing agent. Initially, 790 mL of deionised water and 400 mg of catalyst were fed into the reactor, the magnetic stirrer was adjusted to 700 rpm and the gas mixture of carbon dioxide and hydrogen ($H_2 + CO_2$ (1:1), flow rate = 200 Ncm³/min) was passed through the reactor during 15 min to remove air; CO_2 acts as pH buffer (pH 5.5). Then, 10 mL of a nitrate solution, prepared from $NaNO_3$, was added to the reactor, in order to obtain an initial NO_3^- concentration equal to 100 ppm. Preliminary studies were carried out varying the stirring rate and it was checked that under the selected conditions used there was no external diffusional limitations.

Small samples were taken from the reactor for quantification of nitrate, nitrite and ammonium concentrations after defined periods. Nitrate and nitrite ions were simultaneously determined by HPLC using a Hitachi Elite Lachrom apparatus equipped with a diode array detector. The stationary phase was a Hamilton PRP-X100 column (150 mm × 4.1 mm) working at room temperature, under isocratic conditions. The mobile phase was a solution of 0.1 M NaCl:CH_3OH (45:55). Ammonium ions were determined by potentiometry using a convenient selective electrode. pH values were also measured.

Selected experiments were carried out in duplicate and the results were founded to be reproducible with a maximum error of ca. 2.5% relatively to the conversion average.

The selectivities (also named relative yields) into nitrite, ammonium and nitrogen were calculated as:

$$S_{NO_2^-} = \frac{n_{NO_2^-}}{n_{NO_3^- i} - n_{NO_3^-}} \tag{1}$$

$$S_{NH_4^+} = \frac{n_{NH_4^+}}{n_{NO_3^- i} - n_{NO_3^-}} \tag{2}$$

$$S_{N_2} = \frac{2 \times n_{N_2}}{n_{NO_3^- i} - n_{NO_3^-}} \tag{3}$$

where $n_{NO_3^- i}$ is the initial amount of nitrate (mmol) and $n_{NO_3^-}$, $n_{NO_2^-}$, $n_{NH_4^+}$ and n_{N_2} are the amounts of the respective species (mmol) at time t (min). The amount of nitrogen was calculated by a mole balance, assuming that the amount of NO_x produced is negligible [1,27].

3. Results and discussion

3.1. Catalysts characterization

3.1.1. Hydrogen chemisorption
From these experiments it was possible to obtain the metal dispersion for the monometallic catalyst (see Table 1 in Ref. [25]). For the bimetallic catalysts no hydrogen chemisorption was noticed, which may be an indication that some interaction exists between the noble metal and copper (forming an alloy) or/and copper is covering most of the noble metal strongly limiting hydrogen chemisorption.

Table 1
Textural characterization of the activated carbon (ACo) and some of the catalysts.

Sample	S_{BET} (m²/g)	S_{meso} [a] (m²/g)	V_{micro} [a] (cm³/g)	W_{01} [b] (cm³/g)	W_{02} [b] (cm³/g)	L_1 [c] (nm)
ACo	869	97	0.318	0.290	0.035	0.93
2%Pd–1%Cu_ACo	870	90	0.330	0.295	0.037	0.93
2%Pt–1%Cu_ACo	848	90	0.313	0.287	0.032	0.94

[a] Micropore volume (V_{micro}) and mesopore surface area (S_{meso}) calculated by the t-method.

[b] W_{01} and W_{02} are the micropore volumes associated to small and large micropores, respectively.

[c] Average small micropores width (assuming slit-shaped geometry).

3.1.2. Textural properties

Textural properties obtained from the N_2 adsorption isotherms at 77 K for the activated carbon and for the catalysts with 2% of Pd or Pt are presented in Table 1.

Table 1 shows that the BET surface area of the support is 869 m²/g and it can be observed that for the samples 2%Pd–1%Cu and 2%Pt–1%Cu the textural parameters remained practically unchanged compared to the unloaded carbon. Therefore, it was assumed that the textural properties of the supported metal catalysts are not significantly different from those of the original activated carbon.

3.1.3. TEM

TEM micrographs were collected in order to get information about the metal particle size distributions.
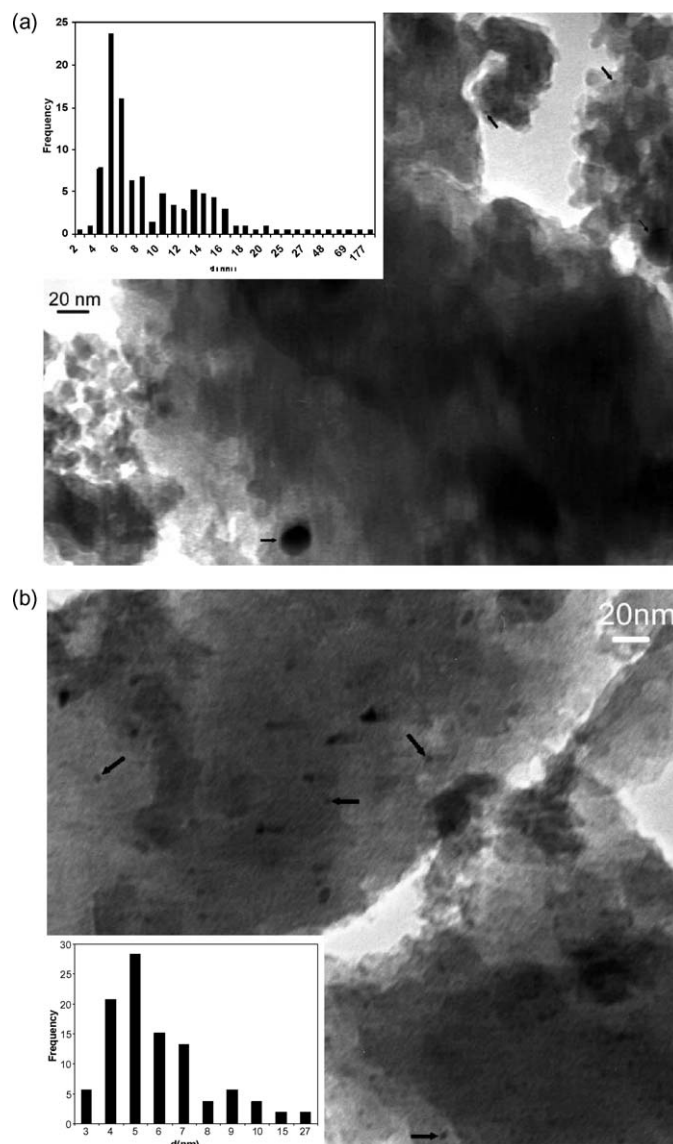
Selected TEM micrographs of the Pd–Cu catalysts are shown in Fig. 1. The metals are well dispersed on the support and the mode diameter (the most frequent value) is 3 nm for the catalyst 1%Pd–0.1%Cu, 5 nm for the catalysts 1%Pd–0.3 and 0.6%Cu and 4 nm for the remaining Pd–Cu samples. Although most of the particles diameter are in the range of 3–7 nm, some larger particles are also presented as can be seen in the micrographs. Barrabés et al. [3], varying the composition of Pd–Cu catalysts supported on a different type of activated carbon, did not observe significant differences in the metal particle sizes. Contrarily, Matatov-Meytal and Sheintuch [18] reported that an increase in the Cu:Pd atomic ratio led to larger metal particles supported on an activated carbon cloth.

For the pairs Pt–Cu, Rh–Cu and Ir–Cu, TEM micrographs were obtained for the most active catalysts and for the catalysts with higher amount of metals. TEM micrographs of the most active catalysts are shown in Fig. 2.

It can be observed that there are no significant differences in the metal particle size, despite the difference in the metals amount. In general, the metal particles are well dispersed. The pair Pt–Cu presents the largest particles, although the majority is in the range 4–6 nm. For the pairs Rh–Cu and Ir–Cu most of the particles have a diameter between 3 and 5 nm. With exception of the catalyst 2%Ir–1%Cu, which presents a mode diameter of 5 nm (results not shown), all the others catalysts present a mode diameter of 4 nm.

3.1.4. XRD

Selected catalysts were analyzed by XRD. XRD spectra of bimetallic catalysts (Figs. 3 and 4) do not show any intense peak of both metals, which could be due to the low amount of metal loaded or could be taken as an indication of a good metal dispersion on the support. TEM images support this last conclusion. The characteristic peaks of the metals can be observed in the XRD spectra of the monometallic catalysts. In addition, in the XRD spectra of the bimetallic catalysts, the peaks of Pd and Pt, when visible, are slightly displaced to the right, which could be indicative of the formation of alloys.

Fig. 1. TEM micrographs of (a) 1%Pd–0.3%Cu_ACo, (b) 1%Pd–0.6%Cu_ACo catalysts.

3.2. Catalytic activity and selectivity

The four catalytic systems Pd–Cu, Pt–Cu, Rh–Cu, and Ir–Cu were evaluated maintaining constant the content of noble metal at 1 wt% and varying the copper content at 0.1, 0.3, 0.6 or 1 wt%. The composition with 2 wt% of noble metal and 1 wt% of Cu was also checked for all the systems studied. For the pairs Pd–Cu and Rh–Cu the compositions with 1 wt% of noble metal and 2% or 5 wt% of Cu were also analyzed. It was found that the catalytic activity and the selectivities are quite different depending on the catalyst composition. All the monometallic catalysts tested are inactive for the nitrate reduction; therefore the presence of bimetallic catalyst is mandatory to reduce nitrate. Nitrite is a reaction intermediate; therefore, its concentration curves generally present a maximum at intermediate reaction times.

3.2.1. Pd–Cu catalysts

Fig. 5 shows the results obtained for the reduction of nitrates over the Pd–Cu catalysts and presents the corresponding evolution of nitrite and ammonium concentrations.

For the catalysts with 1%Pd, there is an increase in the catalytic activity for nitrate reduction with the copper content up to 0.6 wt%,
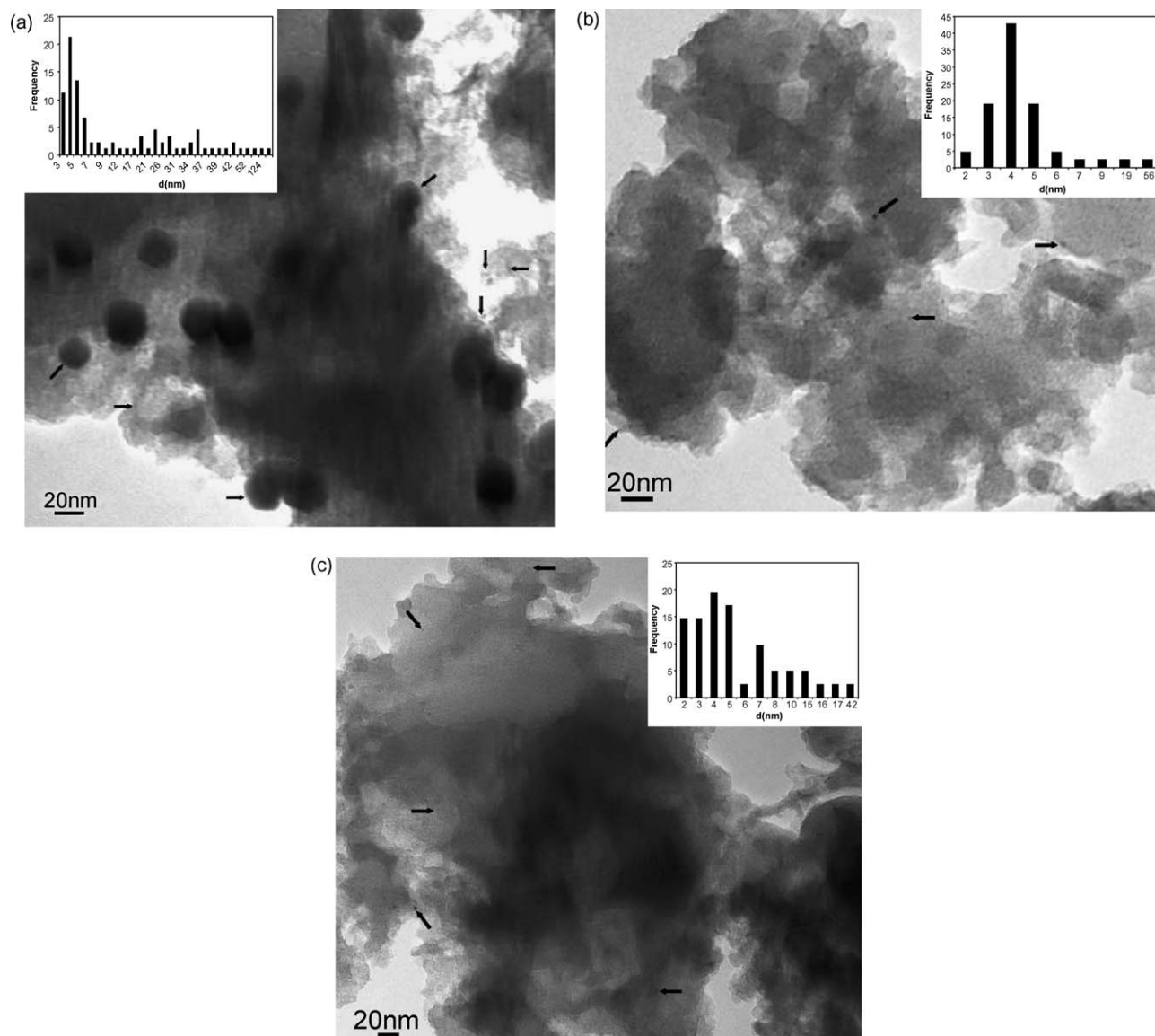
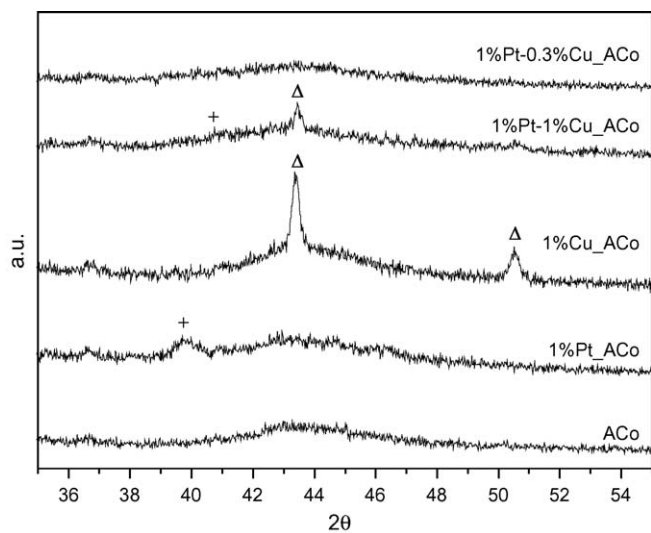**Fig. 2.** TEM micrographs of (a) 1%Pt–0.3%Cu_ACo, (b) 1%Rh–0.6%Cu_ACo and (c) 1%Ir–0.3%Cu_ACo catalysts.

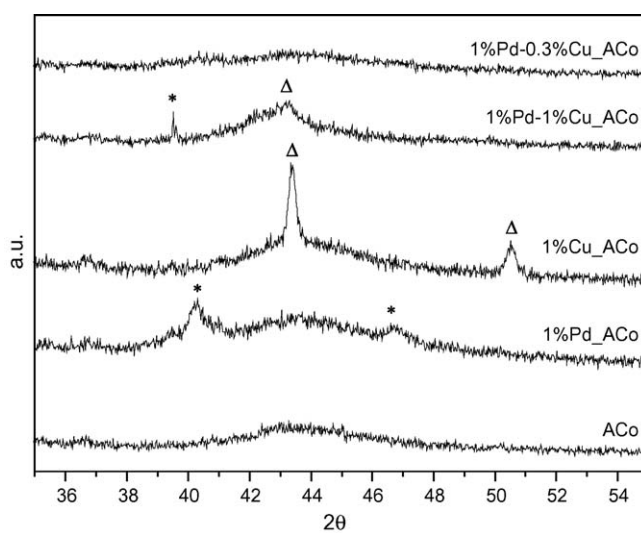**Fig. 3.** XRD spectra of bimetallic Pt–Cu and monometallic Pt and Cu catalysts. Copper ($\triangle$), platinum (+).

Fig. 4. XRD spectra of bimetallic Pd–Cu and monometallic Pd and Cu catalysts. Copper ($\triangle$), palladium (*).
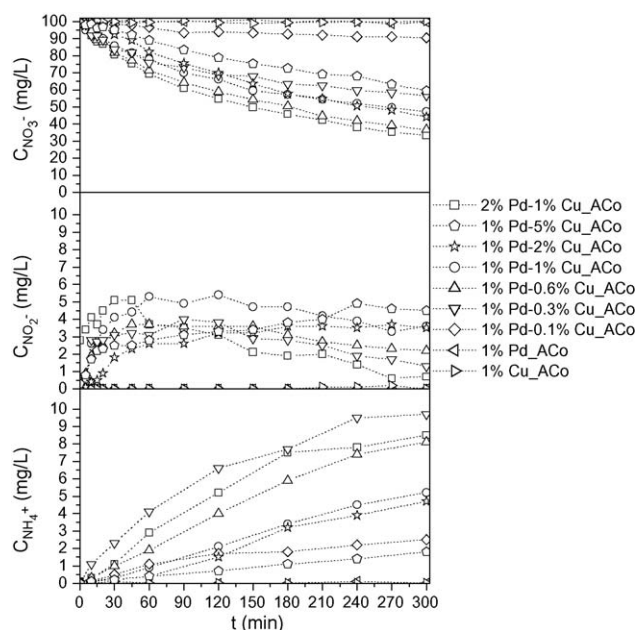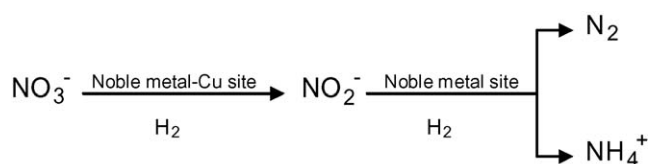
Fig. 5. NO_3^-, NO_2^- and NH_4^+ concentrations as a function of time during nitrate reduction in the presence of Pd–Cu catalysts ($C_{NO_3^- - i} = 100$ mg/L, catalyst = 0.5 g/L, pH 5.5, $Q_{H_2} = 100$ Ncm^3/min, $Q_{CO_2} = 100$ Ncm^3/min, $T = 25$ °C).

which corresponds to an atomic ratio Pd/Cu close to 1, decreasing thereafter. The increase of palladium content to 2%, keeping the copper content at 1%, also increases the nitrate conversion. The order of nitrate conversions after 300 min is the following: 2%Pd–1%Cu > 1%Pd–0.6%Cu > 1%Pd–2%Cu > 1%Pd–1%Cu > 1%Pd–0.3%Cu > 1%Pd–5%Cu ≫ 1%Pd–0.1%Cu.

As expected, considering the well accepted reaction scheme:

$$NO_3^- \xrightarrow[\substack{\text{Noble metal-Cu site} \\ H_2}]{} NO_2^- \xrightarrow[\substack{\text{Noble metal site} \\ H_2}]{} \begin{array}{c} N_2 \\ NH_4^+ \end{array}$$

the nitrite concentration goes through a maximum and the ammonium concentration increases with the nitrate conversion. The catalyst 2%Pd–1%Cu presents the highest nitrate conversion; compared to the other catalysts the maximum in the nitrite formation is obtained for shorter reaction times, which means that nitrite is more rapidly converted into ammonium and nitrogen. This is probably related to the content of palladium. Actually, considering that palladium is highly active for nitrite reduction [25], increasing its content increases the corresponding removal rate.

Matatov-Meytal and Sheintuch [18] reported that the composition of 2%Pd–0.6%Cu (Cu:Pd atomic ratio ≈0.5) is the optimal

content when activated cloth was used as a support; nevertheless, this observation is not in agreement with the results obtained by Barrabés et al. [3], for the same metals supported on activated carbon, who have found the optimum composition of 1%Pd–1%Cu (Cu:Pd atomic ratio ≈1.7). However, they observed that more than a half of the converted nitrate was transformed into nitrite for this catalyst. Our results demonstrate that with this catalyst the concentrations of nitrite are lower than those obtained with the catalysts Pt–Cu (see Section 3.2.2). This is explained by the fact that palladium is more active than platinum for the nitrite reduction [25] and therefore the nitrite formed are more rapidly reduced.

Considering that there are no significant differences on the metal particle size supported on the activated carbon (Fig. 1), the lost of activity with the increase of copper content above 0.6 wt% cannot be explained by the increase of the particles size but probably by the atomic arrangement of the active particles on the surface of the catalysts.

Table 2 shows that the selectivity to nitrogen has a tendency to increase with the increase of copper content. The most selective catalysts to nitrogen are the 1%Pd–5%Cu after 300 min of reaction and the 1%Pd–2%Cu for 20% of nitrate conversion. The catalyst is more active when the metals are in the same atomic proportion (1%Pd–0.6%Cu); however, the catalyst is more selective to nitrogen when the atomic copper content is higher than the atomic palladium content. Yoshinaga et al. [1], suggested that isolated Pd atoms are active sites for the ammonium formation. In fact Table 2 shows that ammonium selectivity increases with the relative amount of palladium content. Moreover, the catalyst 1%Pd–0.1%Cu is highly selective to ammonium, despite presenting small nitrate conversion (cf. Fig. 1). It can be concluded that the selectivity to nitrogen is highly dependent on the copper content. It is well established that nitrite reduction occurs mainly on the noble monometallic sites [5,23], and according to our results it can be considered that there are more isolated particles of the noble metal when the relative quantity of copper is lower. When the noble metal is present in higher amounts than copper, it is expected that the surface of free noble metal is also high and, as the noble metal is very active for hydrogenation reactions, the nitrite molecules are deeply hydrogenated (producing ammonium). When the atomic copper content is close or higher than 50% the noble metal and copper particles are probably not isolated but intercalated or superimposed favouring that the surface nitrogenated intermediates resulting from the nitrate hydrogenation can be combined producing nitrogen molecules instead of being deeply hydrogenated into ammonium.

3.2.2. Pt–Cu catalysts

Fig. 6 shows the evolution of nitrate, nitrite and ammonium concentration in the presence of Pt–Cu catalysts. The catalytic activity and the selectivities are quite different depending on the Pt–Cu contents. For the catalysts with 1%Pt there is an increase in the nitrate conversion when copper contents increases until 0.3%,

Table 2
NO_3^- conversion and selectivities into NO_2^-, NH_4^+ and N_2 after 300 min of reaction and selectivities for 20% of nitrate conversion in the presence of Pd–Cu catalysts.

| Catalyst (wt%)	Cu% atomic	$t = 300$ min				$X_{NO_3^-} = 20\%$		
		$X_{NO_3^- - f}$	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}
1%Pd_ACo	0	0.00	–	–	–	–	–	–
1%Cu_ACo	100	0.00	–	–	–	–	–	–
2%Pd–1%Cu_ACo	45.6	0.67	0.01	0.44	0.55	0.35	0.22	0.43
1%Pd–5%Cu_ACo	89.3	0.40	0.15	0.15	0.70	0.22	0.12	0.66
1%Pd–2%Cu_ACo	77.0	0.56	0.08	0.29	0.62	0.19	0.10	0.71
1%Pd–1%Cu_ACo	62.6	0.52	0.09	0.34	0.56	0.35	0.13	0.52
1%Pd–0.6%Cu_ACo	50.1	0.63	0.05	0.44	0.52	0.23	0.19	0.58
1%Pd–0.3%Cu_ACo	33.4	0.44	0.04	0.74	0.22	0.18	0.52	0.30
1%Pd–0.1%Cu_ACo	14.3	0.09	0.00	0.96	0.04	–	–	–
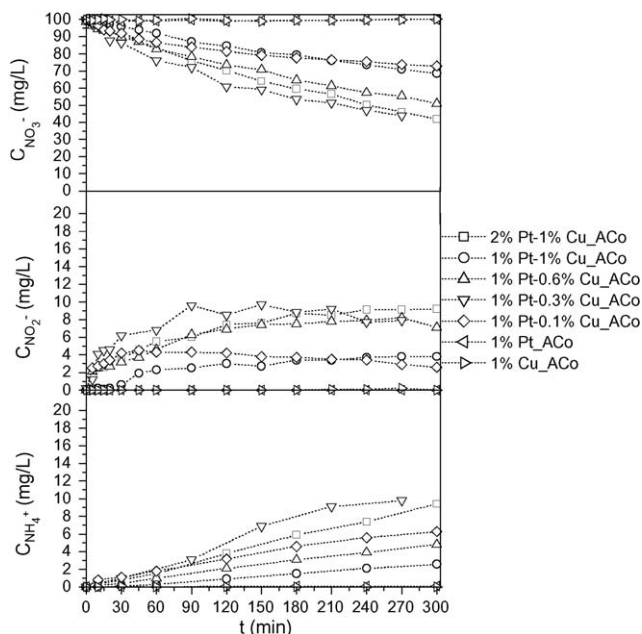
Fig. 6. NO_3^-, NO_2^- and NH_4^+ concentrations as a function of time during nitrate reduction in the presence of Pt–Cu catalysts ($C_{NO_3^-i} = 100$ mg/L, catalyst = 0.5 g/L, pH 5.5, $Q_{H_2} = 100$ Ncm^3/min, $Q_{CO_2} = 100$ Ncm^3/min, $T = 25$ °C).
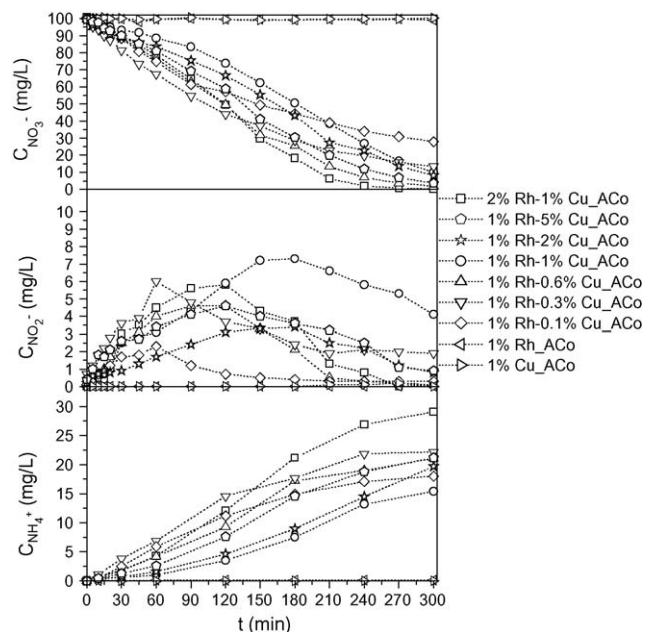
which corresponds to an atomic ratio noble metal/copper close to 1; then a decrease in the conversion was observed for higher amounts of Cu. The catalysts 2%Pt–1%Cu and 1%Pt–0.3%Cu present similar nitrate conversions. The order of nitrate conversions is the following: 1%Pt–0.3%Cu ≈ 2%Pt–1%Cu > 1%Pt–0.6%Cu > 1%Pt–1%Cu ≈ 1%Pt–0.1%Cu. The maximum activity obtained (Cu:Pt atomic ratio ≈ 1) is in agreement with the results reported for the same metals supported on activated carbon by Barrabés et al. [3] and supported on alumina by Epron et al. [23].

The nitrite concentration increases to a certain value, and, after 5 h, is generally higher than that obtained with the pairs Pd–Cu, Rh–Cu and Ir–Cu. This could be related to the fact that Pd and Ir are more active for the nitrite conversion [25] than the Pt. On the other hand, the nitrite concentration goes through a maximum in the case of Pd–Cu (cf. Fig. 5) and Rh–Cu (cf. Fig. 7) but in the case of Pt–Cu (cf. Fig. 6) and Ir–Cu (cf. Fig. 8) the nitrite concentration remains almost constant after a short reaction time.

Table 3 shows that the catalyst 1%Pt–1%Cu is the most selective to nitrogen and, for the catalysts with 1%Pt, the selectivity to ammonium decreases with the increase of copper content. This result is different from that obtained by Epron et al. [23], who observed the opposite performance for the same metals supported on alumina. In our opinion, if part of the noble metal is isolated, their atoms are active sites for ammonium formation and it explains the high ammonium selectivity observed for high Pt/Cu ratios as is the case of the catalyst 1%Pt–0.1%Cu. For the samples 1%Pd–1%Cu and 1%Pt–1%Cu the selectivity to nitrogen after 5 h is similar despite the lower nitrate conversion for the pair Pt–Cu.

3.2.3. Rh–Cu catalysts

Fig. 7 shows the results for the catalysts containing Rh–Cu. In general, the extent of nitrate reduction is higher with these catalysts than with the other pairs studied. Even the catalyst with 1%Rh and just 0.1% of Cu is very active ($X_{NO_3^-} = 72\%$, after 300 min). All the other catalysts with 1%Rh present nitrate conversions between 90 and 98% after 5 h of reaction, being the sample 1%Rh–0.6% the most active. The catalyst with 2%Rh–1%Cu provides the highest nitrate conversion. The catalyst 1%Rh–1%Cu presents a different performance compared to the other

catalysts. For intermediate times, the nitrate conversion obtained with this catalyst is lower than with the others but, after 210 and 270 min becomes higher than those of samples 1%Rh–0.1%Cu and 1%Rh–0.3%Cu catalysts, respectively. This experiment was repeated and the observed behaviour was confirmed.

The Rh–Cu catalysts are the most active for the nitrate conversion among the catalysts tested, but unfortunately, they originate the highest ammonium concentration. Actually, in Table 4 it can be observed that the catalysts Rh–Cu are highly selective to ammonium. The lower selectivity to ammonium was obtained with the catalyst 1%Rh–1%Cu after 300 min of reaction and with the catalyst 1%Rh–2%Cu after 20% of nitrate conversion. As shown in Fig. 7, the catalyst 1%Rh–0.6%Cu is more active than

Fig. 7. NO_3^-, NO_2^- and NH_4^+ concentrations as a function of time during nitrate reduction in the presence of Rh–Cu catalysts ($C_{NO_3^-i} = 100$ mg/L, catalyst = 0.5 g/L, pH 5.5, $Q_{H_2} = 100$ Ncm^3/min, $Q_{CO_2} = 100$ Ncm^3/min, $T = 25$ °C).
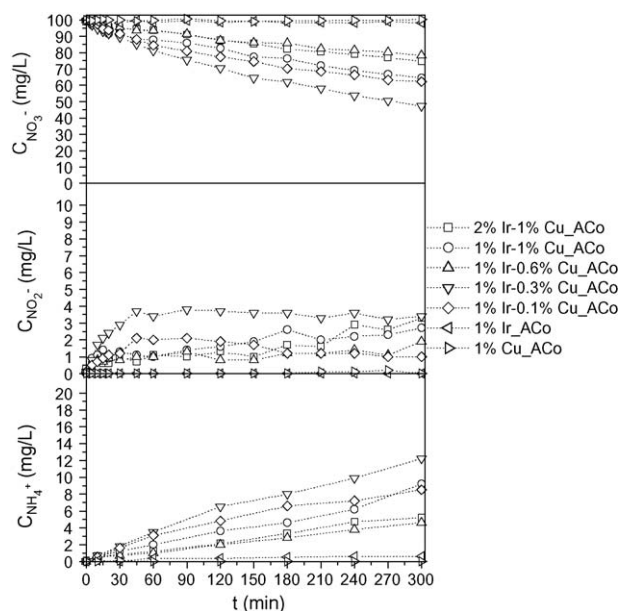

Fig. 8. NO_3^-, NO_2^- and NH_4^+ concentrations as a function of time during nitrate reduction in the presence of Ir–Cu catalysts ($C_{NO_3^-i} = 100$ mg/L, catalyst = 0.5 g/L, pH 5.5, $Q_{H_2} = 100$ Ncm^3/min, $Q_{CO_2} = 100$ Ncm^3/min, $T = 25$ °C).

Table 3

NO_3^- conversion and selectivities into NO_2^-, NH_4^+ and N_2 after 300 min of reaction and selectivities for 20% of nitrate conversion in the presence of Pt–Cu catalysts.

Catalyst (wt%)	Cu% atomic	t = 300 min				$X_{NO_3^-}$ = 20%		
		$X_{NO_3^- f}$	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}
1%Pt_ACo	0	0.00	–	–	–	–	–	–
1%Cu_ACo	100	0.00	–	–	–	–	–	–
2%Pt–1%Cu_ACo	60.6	0.58	0.21	0.56	0.23	0.42	0.34	0.24
1%Pt–1%Cu_ACo	75.4	0.31	0.17	0.29	0.54	0.23	0.27	0.50
1%Pt–0.6%Cu_ACo	64.8	0.48	0.20	0.34	0.46	0.38	0.23	0.39
1%Pt–0.3%Cu_ACo	47.9	0.56	0.19	0.51	0.30	0.56	0.34	0.10
1%Pt–0.1%Cu_ACo	23.5	0.27	0.13	0.79	0.08	0.28	0.63	0.09

Table 4

NO_3^- conversion and selectivities into NO_2^-, NH_4^+ and N_2 after 300 min of reaction and selectivities for 20% of nitrate conversion in the presence of Rh–Cu catalysts.

Catalyst (wt%)	Cu% atomic	t = 300 min				$X_{NO_3^-}$ = 20%		
		$X_{NO_3^- f}$	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}
1%Rh_ACo	0	0.00	–	–	–	–	–	–
1%Cu_ACo	100	0.00	–	–	–	–	–	–
2%Rh–1%Cu_ACo	44.7	1.00	0.00	1.00	0.00	0.27	0.65	0.08
1%Rh–5%Cu_ACo	89.0	0.97	0.01	0.76	0.23	0.25	0.49	0.26
1%Rh–2%Cu_ACo	76.4	0.92	0.01	0.74	0.25	0.15	0.39	0.46
1%Rh–1%Cu_ACo	61.8	0.90	0.06	0.59	0.35	0.34	0.40	0.26
1%Rh–0.6%Cu_ACo	49.3	0.98	0.00	0.74	0.26	0.25	0.62	0.13
1%Rh–0.3%Cu_ACo	32.7	0.90	0.03	0.97	0.00	0.26	0.73	0.01
1%Rh–0.1%Cu_ACo	13.9	0.72	0.01	0.86	0.14	0.15	0.80	0.05

the catalyst 1%Rh–0.3%Cu; however, the latter is more selective to ammonium. Once again, it can be concluded that the selectivity to nitrogen is highly dependent on the copper content, and as well as observed for the catalysts Pd–Cu and Pt–Cu the highest selectivity to nitrogen is obtained for the catalysts with atomic copper contents higher than 50%. Also as in the previous systems, the highest activity in nitrate reduction is obtained for the catalyst with an atomic ratio noble metal/copper close to 1.

3.2.4. Ir–Cu catalysts

Fig. 8 shows the results obtained for the reduction of nitrates over Ir–Cu catalysts as well as the corresponding evolution of nitrite and ammonium concentrations during the reaction. It is observed that the catalytic activity is quite different depending on the Ir–Cu content ratio. As observed for the Pt–Cu catalysts (Fig. 6) the most active formulation for the Ir–Cu catalysts is that with 0.3% of Cu, which corresponds to an atomic ratio noble metal/copper close to 1. However, in this case, a direct relationship with the metals content cannot be established, because the nitrate conversion obtained does not follow a tendency. The order of nitrate conversions is the following: 1%Ir–0.3%Cu > 1%Ir–0.1%Cu ≥ 1%Ir–1%Cu > 2%Ir–1%Cu ≥ 1%Ir–0.6%Cu. The monometallic catalyst with 1%Ir is practically inactive for the nitrate reduction, since a 2% conversion after 5 h was obtained but only nitrite was detected in the liquid mixture. Fig. 8 shows that the concentration of nitrite increases as nitrate conversion increases

only in the beginning of reaction and thereafter remains almost constant. On the other hand, the concentration of ammonium increases with the nitrate conversion and with reaction time. It was observed previously [25] that, after the palladium catalyst, the iridium catalyst is the most active for the nitrite conversion but it was the most selective to ammonium. Probably, this explains the higher NH_4^+ selectivities obtained with the iridium catalysts. Indeed, Table 5 shows that the Ir–Cu catalysts are highly selective to ammonium. The catalysts 1%Pt–0.3%Cu and 1%Ir–0.3%Cu (cf. Figs. 6 and 8, respectively) present similar nitrate conversions after 5 h of reaction; however, it is possible to see in Table 5 that the catalyst with Ir is much more selective to ammonium than the catalyst with Pt (see also Table 3). It is interesting to note that only for the iridium-containing catalysts the selectivity to ammonium remains almost unchanged for different ratios noble metal/copper (cf. Fig. 9).

3.2.5. Summary of the catalytic activity and selectivity results

Fig. 9 summarizes the results obtained for nitrates conversion and selectivities to ammonium and nitrogen for all the catalysts tested as a function of atomic copper content.

The results compiled in this figure clearly indicate that both activity and selectivities are strongly affected by the type of metal pairs and also by the metals contents ratio. The Rh–Cu catalysts provide the highest nitrate conversions. For all pairs there is an increase in the nitrate conversion when copper contents increases:

Table 5

NO_3^- conversion and selectivities into NO_2^-, NH_4^+ and N_2 after 300 min of reaction and selectivities for 20% of nitrate conversion in the presence of Ir–Cu catalysts.

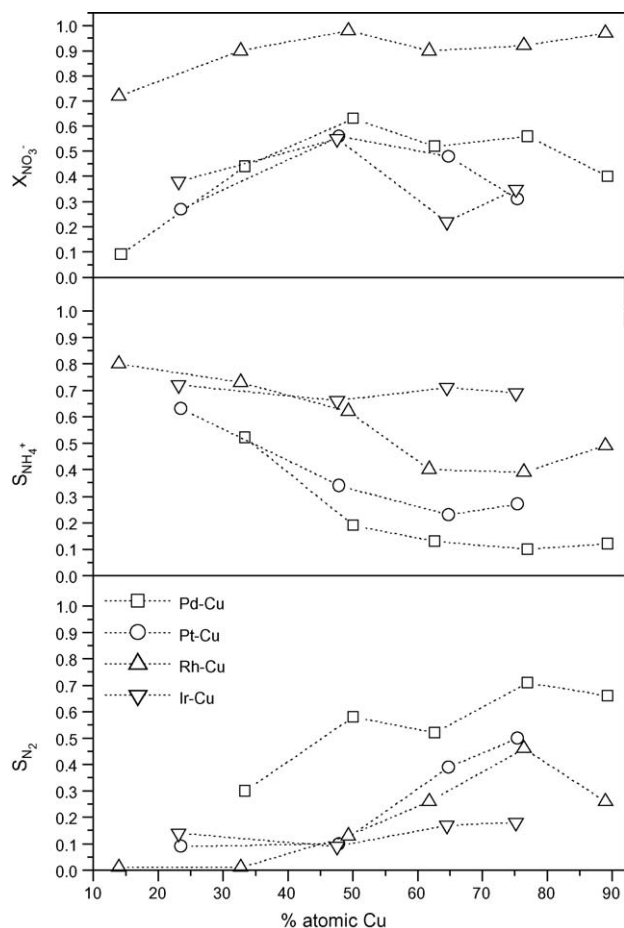| Catalyst (wt%)	Cu% atomic	t = 300 min				$X_{NO_3^-}$ = 20%		
		$X_{NO_3^- f}$	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}	$S_{NO_2^-}$	$S_{NH_4^+}$	S_{N_2}
1%Ir_ACo	0	0.02	0.00	1.00	0.00	–	–	–
1%Cu_ACo	100	0.00	–	–	–	–	–	–
2%Ir–1%Cu_ACo	60.2	0.25	0.18	0.73	0.09	0.20	0.79	0.09
1% Ir–1%Cu_ACo	75.2	0.35	0.10	0.89	0.01	0.13	0.69	0.18
1% Ir–0.6%Cu_ACo	64.5	0.22	0.11	0.72	0.17	0.12	0.71	0.17
1% Ir–0.3%Cu_ACo	47.6	0.55	0.09	0.81	0.10	0.25	0.66	0.09
1% Ir–0.1%Cu_ACo	23.2	0.38	0.04	0.78	0.18	0.14	0.72	0.14

Fig. 9. NO_3^- conversion after 5 h of reaction and NH_4^+ and N_2 selectivities at 20% of nitrate conversion as a function of % atomic of copper for the catalysts with 1 wt% of noble metal.

up to 0.3% for Pt–Cu and Ir–Cu catalysts and 0.6% for Pd–Cu and Rh–Cu catalysts, decreasing thereafter. These maxima in nitrate conversion correspond to an atomic ratio of noble metal/copper approximately equal to 1, indicating that the same amount of metal atoms is the best formulation to achieve a very active catalyst for this reaction. The selectivity to nitrogen increases with the atomic copper content, at least up to ca. 75% and it seems to decrease thereafter at least for Pd and Rh containing catalysts. The opposite is generally observed for the selectivity to ammonium, showing that with the increase of copper content the accessible surface of free noble metal, which is known to be very active for ammonium production, decreases. The Ir catalysts are the exception because their selectivity to ammonium is practically independent of the Cu content and always high. The pair Pd–Cu is the most selective in the transformation of nitrate to nitrogen compared to the pairs Pt–Cu and Rh–Cu, which present similar nitrogen selectivities, and to the Ir–Cu pair.

All the catalyst tested in this work were calcined and reduced at 400 °C. At this high temperature some alloy formation may occur. The XRD results and the fact that no hydrogen chemisorption was observed for the bimetallic catalysts, contrary to the monometallic catalysts, seem to support this observation. The possibility of alloy formation in the different catalytic systems could be responsible for the relatively low selectivity to nitrogen observed (the maximum obtained was around 70% for the Pd–Cu catalyst). Therefore, further studies on the influence of the calcination and reduction temperatures during catalysts preparation in the possibility of alloy formation and consequently in the selectivity to nitrogen are currently being carried out.

4. Conclusions

A detailed study on the influence of the metals composition of the bimetallic systems Pd–Cu, Pt–Cu, Ir–Cu, and Rh–Cu supported on activated carbon as catalysts for the nitrate reduction with hydrogen in water was carried out. The pairs Ir–Cu and Rh–Cu were assessed for the first time.

The monometallic catalysts are inactive (Pd, Pt, Rh, and Cu) or practically inactive (Ir) for the reduction of nitrate.

The activity of the catalysts is quite different depending on the copper content. For all the catalysts tested, the maximum activity was obtained for an atomic ratio noble metal/copper close to 1, which is indicative that the same amount of noble metal and promoter atoms is the best formulation to obtain a very active catalyst for this reaction.

Rh–Cu bimetallic catalysts are the most active among the catalysts tested, usually more than 90% of nitrate conversion being obtained after 5 h of reaction. However, significant amounts of ammonium are obtained.

The pair Pd–Cu was the second most active system studied, reaching around 60% of nitrate conversion. Generally, the pairs Ir–Cu and Pt–Cu are less active and present similar nitrate conversions, but the former presents higher selectivities to ammonium.

There is a trend of the selectivity to nitrogen to increase with the increase of the atomic copper content up to 75%. This is valid for all the systems tested, with the exception of the pair Ir–Cu where the selectivity to ammonium is always high and practically independent of the metals composition.

The pair Pd–Cu is the most selective in the transformation of nitrate to nitrogen when compared to the other systems.

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